

UDC 666.613:642.7

STRUCTURE FORMATION IN DENSELY SINTERED HOUSEHOLD CERAMICS

I. A. Levitskii¹ and Yu. A. Klimosh¹

Translated from *Steklo i Keramika*, No. 6, pp. 32 – 36, June, 2005.

The formation specifics of the structure and phase composition of densely sintered ceramics based on a low-melting argillaceous material from Belarus together with a combined flux and a grog additive are investigated. The correlation between the physicochemical properties, structure, phase composition, and the time-temperature firing schedules of the developed materials are investigated. Electron probe microanalysis makes it possible to monitor variations in the chemical composition at various local sites and compare it with the estimated composition of the mixture. The optimum regimes for the heat treatment of articles are determined.

An important place among ceramic materials with a wide range of technical and specific properties is occupied by ceramics made of densely sintered mixtures intended for operating in contact with different alimentary media (alkali and acid solutions, alcoholic drinks). Densely sintered ceramics used for household food containers has several advantages, such as gas- and water impermeability, resistance to aggressive media, and high heat resistance.

Production of densely sintered household ceramics in Belarus is practically nonexistent. Such products are imported from Russia, Germany, and other countries. This is mainly related to the lack of high-melting refractory argillaceous materials in the republic and the absence of efficient fluxing components (nepheline-sienite, talc, perlite, etc.). However, densely sintered materials with good service properties can be produced on the basis of low-melting argillaceous materials subject to a rational combination of ceramic mixture components and technological parameters for producing articles based on them [1, 2].

The structure and properties of ceramic materials to a large extent reflect the physicochemical processes occurring in firing. Various phase transformations, crystallization processes, the structure of the emerging liquid phase, the qualitative and quantitative composition of the system, the rate of heating and cooling of samples, the duration of isothermal exposure at the maximum temperature, and several other factors have a substantial effect on the structure formation of ceramic materials and, accordingly, on its properties.

The purpose of our study is the investigation of structure and phase formation specifics in densely sintered ceramic mixtures based on low-melting clays of Belarus for the pur-

pose of identifying optimum heat treatment conditions to ensure steady and isotropic properties and phase composition over the whole volume of ceramic samples.

We have investigated ceramic mixtures using low-melting clays from the Gaidukovka deposit (Minsk Region) and Lukoml' deposit (Vitebsk Region) as plastic components, with a small (10%; here and elsewhere wt.%) additive of refractory clay from the Latnenskoe deposit (Russia). The fluxing component was a combined flux (nepheline-sienite and frit) and the grog component was chamotte refractory scrap. The frit was boroaluminosilicate glass with the following composition (%): 17.80 B₂O₃, 68.00 SiO₂, 4.00 Al₂O₃, 8.90 Na₂O, 1.15 K₂O, 0.12 MgO, and 0.03 CaO (USSR Inventor's Certif. No. 893918) that is used to produce clear glazes for decorating household ceramics.

Experimental mixtures were prepared using the traditional slip technology by joint moist milling of components to a particle size ensuring a residual of 1.5 – 2.0% on a No. 0063 sieve. The relative moisture of the slip after milling was 42 – 45%. To improve the flow properties of slip, we used a complex electrolyte containing soda ash, water glass, sodium tripolyphosphate, and a coal-alkali reactant. The samples were cast into gypsum molds. The preforms were dried naturally to a residual moisture not more than 0.5%. In order to study the specifics of structure formation and the phase composition, the dried samples were fired in electric batch furnaces within a wide temperature interval: 600 – 1050°C. The exposure at the final temperature was 1 – 1.5 h.

The experiments demonstrated that the optimum mixtures have the following composition (%): 60 – 70 low-melting clay, 10 refractory clay, 20 – 30 fluxing additive, and 10 chamotte. The properties of the samples fired in the temperature interval of 1000 – 1050°C were as follows: water

¹ Belarus State Technological University, Minsk, Belarus.

absorption up to 5%, apparent density 2280–2450 kg/m³, open porosity 1.4–9.0%, total shrinkage 3–8%, and CLTE $(63–66) \times 10^{-7} \text{ K}^{-1}$. The optimum water absorption was registered in mixtures containing at least 18% Al₂O₃, at least 17% (R₂O + RO + Fe₂O₃), and the RO : R₂O ratio equal to 1.00–1.25.

The phase composition of the materials synthesized in the temperature interval of 600–800°C is represented by α -quartz, hematite, kaolinite, hydromica, aegirite, and calcite. The intensity of α -quartz peaks in the interval of 700–1050°C with an increasing heat-treatment temperature started decreasing. This can be attributed to the growing amount of the vitreous phase, in which silica dissolves more intensely with increasing temperature and new crystalline phases are formed with the participation of SiO₂. The intensity of the diffraction maxima of kaolinite, calcite, and illite in the interval of 600–800°C decreases, and at a temperature above 800°C they totally decompose with their subsequent partial dissolution in the melt. The intensity of the diffraction maximums of hematite grows up to a temperature of 1000°C and with further increase to the maximal temperature the intensity of hematite peaks decreases due to the transition of Fe₂O₃ into the melt. The intensity of the diffraction maximum of aegirite decreases as well with growing temperature; next, aegirite completely decomposes in the interval of 1000–1050°C with its possible dissolution in the melt.

The crystallization of anorthite starts at a temperature around 800°C and, as the temperature grows to 1050°C, the intensity of the diffraction maxima of this crystalline phase grows. The maximum quantity of anorthite is registered at 1050°C, which improves the properties and, accordingly, the degree of sintering of ceramics.

The microstructure of the samples was investigated using a JSM-5610 LV scanning electron microscope (Japan) and a LEICA-DMLB optical microscope (Germany) with a Sony built-in analog-digital camera. Photos of sample surface and sections have been obtained.

The study of the structure of the synthesized samples by electron microscopy ($\times 500$ and 1000) has demonstrated that it is difficult to morphologically identify quartz anorthite, hematite, and aegirite crystals in the material. The electron microscope photos exhibit structural elements represented by crystals, aggregates of an amorphous argillaceous material of a complex composition, and a substantial amount of the vitreous phase.

More complete data on the structure of the materials were obtained studying polished sections in transmitted light with an optical microscope ($\times 100$). The structure of materials fired at 950°C exhibits randomly located fine anorthite grains with a relict twin structure and cleavage. The total content of anorthite is up to 25%. A small quantity of fine quartz grains of a fragmentary angular shape was registered. The high intensity of quartz diffraction maxima obtained in deciphering diffraction patterns but its small quantity in sections observed visually is presumably due to the fine-crystal-

line structure of quartz that forms the main crystal skeleton of the material. Samples fired at 950°C also have a substantial quantity (up to 25%) of pores of various sizes (20–60 μm) and shapes.

As the heat treatment temperature grows to 1000°C, the consolidation of the material is observed, whereas the quantity and size of the pores significantly decrease. Pores of circular, less frequently of elongated, shape are uniformly distributed. Their total quantity is approximately 10%. The overwhelming majority of pores have a size of 5–20 μm . The bulk of the ceramic material is represented by a vitrified gray-brown component, presumably saturated with iron oxides and hydroxides. The total content of quartz and anorthite is approximately 40%. The size of anorthite crystals is within the limits of 6–8 μm , and that of quartz is 3–6 μm .

As the heat treatment temperature grows to 1050°C, the total quantity of pores decreases to 5–7%. Pores, as a rule, are round, of size 1–10 μm , and are surrounded by clear glass. Isometric or, occasionally, prismatic anorthite crystals with a relict twinning structure and cleavage prevail in the bulk of the material. The anorthite crystals are very fine (up to 3 μm) and mainly fused in their edges. The total content of quartz and anorthite is approximately 40% with the latter prevailing. It should be noted that the bulk material has a more saturated gray-brown color determined by intense melting of iron oxides, in particular, hematite crystals in the melt.

The deformation and swelling of samples takes place under heat treatment above 1050°C due to a substantially growing quantity of the vitreous phase that prevents the products of dehydration and decomposition from leaving the pores.

The electron-probe microanalysis of samples performed using a scanning electron microscope with a system for chemical analysis makes it possible to observe the distribution and concentration of chemical elements in the material and to map their distribution by an electron beam scanning of the sample surface.

The elemental composition was analyzed based on characteristic radiation spectra. The spectra were deciphered by comparing spectral lines with standard ones. The quantitative analysis is based on measuring the ratio of the diffraction intensities of the sample and the known reference standard.

The distribution of elements and, accordingly, the structure of the material change significantly with increasing heat-treatment temperature.

Figure 1 shows a photograph of the surface of the optimum-composition sample (firing temperature 1000°C) selected for microprobing. Table 1 shows the chemical composition of the sample, the averaged chemical composition of the surface of microprobing, as well as the chemical composition calculated using the EXCEL application package.

It should be noted that the chemical composition of the sample surface obtained in the microprobe analysis correlates well with the estimated chemical composition. This shows that the structure and composition of samples are ho-

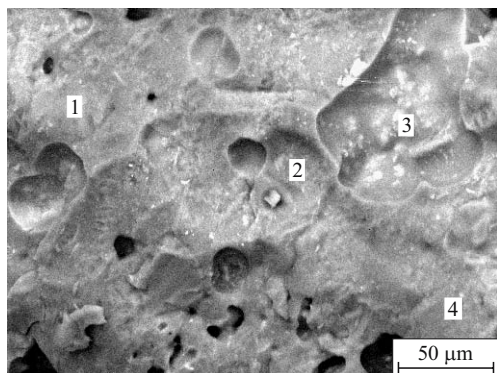


Fig. 1. Electron microscope photograph of a site of the sample surface ($\times 1000$): 1 – 4) local sites of microprobe analysis.

homogeneous. The slight fluctuations in oxide contents within the limits of 0.5 – 1.0% are presumably related to such factors as isomorphous element substitutions in crystalline phases, their structural defects, the presence of impurities, etc. Furthermore, one of the most important conditions of a homogeneous distribution of particular elements is their direct correlation with their quantity.

For microanalysis we selected non-typical structural sites of synthesized materials, such as a crystalline matrix, large pores, fused crystal grains, and crystallized melt, since we wished to determine the chemical composition of all samples sites, as well as inside the pores and on the pore-material interface.

It can be seen in Fig. 1 that the crystalline component of the material is rather well fused and there is a dense fused edge (aureole) around the pores, which is presumably responsible for good properties and water impermeability of the material. Certain fluctuation in the contents of individual oxides have been registered on local sites 1 – 4, which agrees with the map of the distribution of chemical elements. The high concentration of individual elements on certain areas of the map is presumably related to their incorporation into the crystalline formations. Thus, local aggregates of silicon and oxygen are presumably determined by their presence in the composition of the crystalline phase of α -quartz.

A certain increase in the content of low-melting elements (K, Na, Ca, Mg, and B) is registered on the pore boundaries and inside the pores. This indicates that the vitreous phase facilitates the fusing of pores and thus improves the physicochemical properties of the material. The presence of a characteristic edge (aureole) consisting of Si, K, Na, Ca, Mg, and O around the pores is an indication of their presence in the vitreous phase.

Analyzing the quantity of iron oxides on the element distribution map, one can see that it is uniform. According to the results of x-ray phase analysis, the content of hematite in the temperature interval of 1000 – 1050°C decreases, which is related to its melting, transition into the vitreous phase, and, presumably, its uniform distribution in the structure of the material. This is corroborated not only by x-ray phase analysis data, but also by the uniform bulk tinting of the sample. In this case one can assume the transition of Fe^{2+} and Fe^{3+} cations into the vitreous phase together with the above specified cations.

It is known that the structure and phase composition of the material to a large extent depends on the heat treatment conditions, the duration of the isothermal exposure, and the rate of heating and cooling of the samples. We have performed a study to identify the regularities of the variation of physicochemical properties and structure of ceramics under variations of the maximum firing temperature and isothermal exposure at that temperature. To identify the optimum heat treatment regimes, the following isothermal exposure duration was selected for 1000 and 1050°C: 30, 60, and 90 min, which is related to the technological regimes of heat treatment of articles in industrial electric firing furnaces.

It was found in the course of experiments that as the isothermal exposure duration increases, the properties of samples improve significantly. Thus, at a firing temperature of 1000°C with isothermal duration for 30 min, the samples were water-permeable, had sufficiently high water absorption (14.1 – 18.4%), porosity of 27.3 – 34.9%, CLTE $(70.9 - 73.1) \times 10^{-7} \text{ K}^{-1}$, and a low density (1889 – 1935 kg/m^3). As the exposure duration grew to 90 min, the physicochemical properties of samples significantly improved; in particular, they became water-impermeable. The

TABLE 1

Analyzed site	Mass content, %							
	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	$\text{FeO} + \text{Fe}_2\text{O}_3$	B_2O_3
Microprobing surface*	56.40	18.86	6.03	1.51	3.61	5.41	6.46	1.72
Local site:**								
1	53.97	21.62	5.59	1.64	3.16	6.85	5.62	1.55
2	50.82	14.21	6.53	1.37	2.05	12.55	10.79	1.66
3	55.46	24.74	6.74	1.87	3.62	3.72	2.25	1.60
4	61.79	18.46	3.49	0.92	2.78	7.86	3.08	1.63
Estimated mixture content	61.62	18.80	5.13	2.17	3.46	2.70	4.35	1.78

* Microprobing surface is the sample site limited by the area shown in the photograph in Fig. 1.

** 1 – 4) local microprobing sites (see Fig. 1).

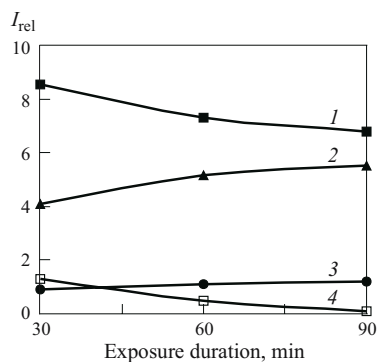


Fig. 2. Dependence of intensity of diffraction maxima of crystalline phases on exposure duration of samples at a temperature of 1000°C: 1) α -quartz ($d = 0.334$ nm); 2) anorthite ($d = 0.318$ nm); 3) hematite ($d = 0.269$ nm); 4) aegirite ($d = 0.297$ nm).

water absorption decreased to 1.9–4.4%, the porosity was 4.4–9.7%, the density was 2208–2312 kg/m³, and the CLTE $(64.2 - 66.3) \times 10^{-7} \text{ K}^{-1}$.

The maximum degree of sintering in investigated mixtures was reached at 1050°C with 60 min exposure: the water absorption of articles was 0.7–1.7%, the density was 2308–2410 kg/m³, the porosity 1.7–3.9%, and the CLTE $(63.5 - 64.7) \times 10^{-7} \text{ K}^{-1}$. Increasing the exposure at this temperature to 90 min resulted in the deformation and swelling of samples due to the expansion of pores, as a consequence of excessive gas pressure, as well as a significant increase in the quantity of the vitreous phase, which prevents the exit of the products of gas formation to the surface of the article.

The analysis of the physicochemical properties of the obtained samples, fuel and energy costs, as well as the parameters of furnaces used at ceramic factories of the republic suggest that for the specified type of ceramics the most advisable regime is firing at 1000°C with a 90-min exposure at the maximum temperature.

According to x-ray phase analysis, the main crystalline phases of samples fired at 1000 and 1050°C with exposures of 30, 60, and 90 min are α -quartz, anorthite, hematite, and aegirite. At a temperature of 1000°C (Fig. 2) the most intense diffraction maxima are registered in α -quartz, which is customary, since the local clays used contains a substantial amount (15–37%) of free quartz. An increase in exposure duration from 30 to 60 min abruptly decreases the diffraction maximum intensities of α -quartz and aegirite and increases the intensity of the crystallization of anorthite, which, in turn, improves the physicochemical properties of samples.

There is no perceptible variation in the maximum diffraction intensities of anorthite, α -quartz, and hematite as the exposure at 1000°C extends from 60 to 90 min; at the same time nearly complete disappearance of aegirite is observed related to its transition into the melt.

The modification of sample structure, as the duration of isothermal exposure at 1000°C extends from 30 to 90 min, is

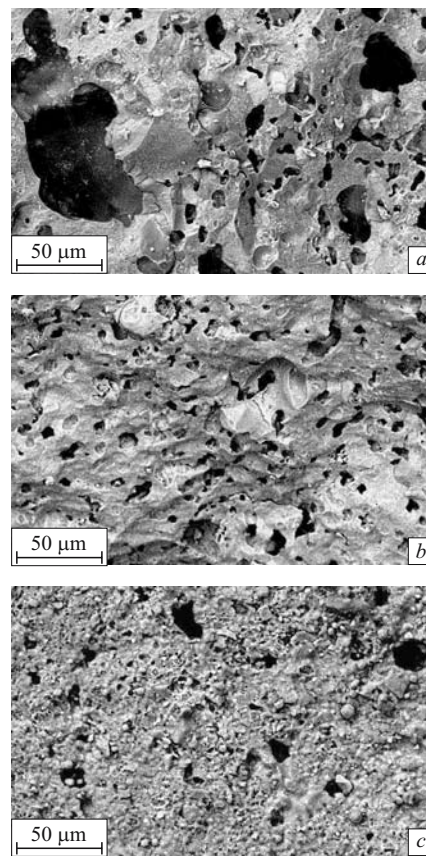


Fig. 3. Electron microscope photographs of a sample surface fired at 1000°C ($\times 500$): a, b, and c) isothermal exposure of 30, 60, and 90 min, respectively.

shown in Fig. 3. It can be seen that under a 30-min exposure the sample, in addition to the crystalline and vitreous phases, exhibits large communicating pores whose content is 20–25%. The pores are prevalently spherical, the size of the large pore ranges within 50–100 μm , and of fine pores, 10–30 μm . As the exposure increases to 90 min, a sharp consolidation of the material takes place and the quantity and size of pores decrease significantly, which is due to the growing amount and viscosity of the vitreous phase facilitating the fusion of pores and the formation of a densely sintered material.

The intensification of sintering processes of the investigated ceramic mixtures in the temperature interval of 1000–1050°C is related to the specifics of their chemical composition. The viscosity and quantity of the vitreous phase, apart from the effect of alkali and alkaline-earth metal oxides introduced with batch components, to a large extent depend on the presence of B_2O_3 (17.5–18.0%) in the frit. It has an active fluxing effect due to the formation of eutectic melts at a low melting temperature and perceptibly decreases the melt viscosity [3].

Furthermore, the intense sintering of mixtures containing substantial quantities of low-melting clays, as isothermal exposures at 1000–1050°C increase, is presumably due to the

active participation of Fe^{2+} and Fe^{3+} ions in the formation of the vitreous phase and their participation in the composition of aluminosilicate eutectics.

Thus, the most significant factors affecting the formation of densely sintered materials based on low-melting clays from Belarus are the sintering conditions of ceramic mixtures: the firing temperature and the isothermal exposure duration. Furthermore, a critical effect on the degree of sintering and the physicochemical properties of the material is exercised by the quantity and viscosity of the vitreous phase, as well as the phase composition of new crystal formations.

Industrial testing at the Belkhudozhkeramika Company has corroborated the justifiability and appropriateness of the

temperature-time regimes proposed for firing ceramic mixtures. The resulting products have maximum water absorption, porosity and apparent density.

REFERENCES

1. V. F. Pavlov, "Methods for sintering intensification and improving ceramic properties," *Steklo Keram.*, No. 8, 14 – 16 (1974).
2. V. F. Pavlov, A. S. Krasnousova, and L. L. Koshlyak, *Use of Low-Melting Clays in Production of Ceramic Tiles on Automated Conveyor Lines* [in Russian], VNIIESM, Moscow (1977).
3. A. A. Appen, *Chemistry of Glass* [in Russian], Khimiya, Leningrad (1970).